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SYNTHESES AND VIBRATIONAL SPECTRA OF CHLOROFLUORAMINES

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SUMMARY

The chlorofluoramines $NFCl_2$ and NF_2Cl were prepared by fluorination of an NH_4Cl-$NaCl$ mixture and characterized by vibrational spectroscopy. For NF_2Cl, two fundamental vibrations were reassigned.

INTRODUCTION

The halogenated amines are in general highly energetic [1, 2]. This characteristic allows the production of excited state species such as nitrenes by either chemical reactions or photolysis [3]. Excited state nitrenes and particularly NF have been studied extensively as a lasing medium but required the use of either halogen azides [4-6] or NF_2 [7] as precursors. Since both of these are difficult to work with, a study was undertaken at the University of Denver to explore the use of chlorofluoramines as an alternate and more convenient source of excited nitrenes. This interest in chlorofluoramines prompted a search for a convenient and safe synthesis of $NFCl_2$ and NF_2Cl, and a reinvestigation of their spectroscopic properties.

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$NFCl_2$ was first prepared [8] in 1963 from NaN_3 and ClF according to:

$$2ClF + NaN_3 \rightarrow NFCl_2 + NaF + N_2$$

However, the formation of highly explosive ClN_3 [9] as a by-product makes this method unattractive and may have been responsible for the reported instability [8] of condensed $NFCl_2$. An alternate synthesis of $NFCl_2$ was reported in 1968 and involved either the chlorination of NH_4F and NaCl-NaF mixtures or the fluorination of NH_4Cl and NaF mixtures [10]. Finally, the formation of $NFCl_2$ was mentioned in a 1969 paper on the chlorination of either ethyl fluorocarbamate or ethyl chlorofluorocarbamate by an excess of aqueous sodium hypochlorite [11]. In this paper, we would like to report on a modified fluorination reaction of NH_4Cl and some spectroscopic properties of $NFCl_2$ and NF_2Cl.

EXPERIMENTAL

Materials and Apparatus. Reagent grade NH_4Cl and NaCl (Barker) were finely ground together prior to use. Fluorine (Air Products) was premixed with dry N_2 in a mole ratio of 1:4, stored in a high pressure Monel cylinder at 1000 psi pressure, and its flowrate controlled by a flowmeter. Accidental overpressurization of the reactor was prevented by installing between the flowmeter and the reactor a blow-out bubbler filled with fluorocarbon oil. The fluorination reactor consisted of a 35 cm long, 3/4 inch o.d. copper tube which was kept at the desired temperature by means of an electric heating tape and temperature controller. The reactor was packed with a 1:1 mixture of NH_4Cl and NaCl dispersed between freshly cleaned dry copper shot. The reactor was followed by a stainless steel tube filled with activated NaF pellets (prepared from $NaHF_2$ pellets by heating to 300°C in a dry N_2 stream) for the removal of HF. The HF scrubber was followed by two Teflon-FEP stainless steel U-traps that were equipped with shut off valves and cooled to -78° and -183°C with a CO_2 bath and liquid Ar, respectively. The second Teflon cold trap was followed by another fluorocarbon oil filled bubbler to prevent back condensation of atmospheric moisture.

Infrared spectra were recorded on a Nicolet Model 5DXC FT IR spectrometer with a resolution of $2cm^{-1}$. The matrix isolation apparatus consisted of a RMC-Cryosystems LTS-22 closed cycle system operated at 8°K and 5×10^{-6} torr pressure. The samples were diluted with Ar to a MR of 100 and deposited through a needle valve on a cold KCl window. Typical deposition times used were two hours. Low temperature Raman spectra were recorded on a Spex Model 1403 spectrometer using the 647.1 nm line of a Kr ion laser and a previously described cooling device [12].

Synthesis of $NFCl_2$ and NF_2Cl. In a typical experiment, the reactor was loaded with 8 grams of NH_4Cl and 8 grams of NaCl dispersed on copper shot. Dry N_2 was passed through the reactor at 110°C for several hours to dry the reactor and the reagents. Then, the temperature was lowered to 55°C, and a mixture of 0.1 mol of F_2 and 0.4 mol of N_2 was passed through the reactor at a flow rate of 100cc/min, followed by a 10 min purge with pure N_2. The -183°C U-trap was transferred to a passivated (with ClF_3) stainless steel-Teflon FEP vacuum line [13], and the -183°C bath was replaced by liquid N_2 (-196°C). The products were separated by fractional condensation in a dynamic vacuum through a series of U-traps kept at -95° (toluene slush), -116° (ethanol slush), -142° (methylcyclopentane slush) and -196°C. The -196°C trap contained essentially pure NF_2Cl (1-2 mmol), the -142°C trap had mainly Cl_2 (6-8 mmol) and some $NFCl_2$ and a trace of NF_2Cl, the -116°C trap contained mainly $NFCl_2$ (~1 mmol) and some Cl_2, while the -95°C trap was essentially empty.

RESULTS AND DISCUSSION

Syntheses of $NFCl_2$ and NF_2Cl. Our synthesis of $NFCl_2$ and NF_2Cl is a modification of that originally reported by Pankratov and Sokolov [10]. It involves the fluorination of NH_4Cl with elemental F_2 in a flow reactor. In our study, it was found that the addition of NaCl to the NH_4Cl significantly increased the yields of the desired chlorofluoramines. Furthermore, careful drying of the reaction system is important to avoid the formation of $FClO_3$ and $FONO_2$. Although the yields of $NFCl_2$ and NF_2Cl are relatively low, and separation of the $NFCl_2$ from the main by-product Cl_2 is difficult and may require repeated careful fractionations, the method is a relatively convenient and safe way to produce moderate amounts of $NFCl_2$ and NF_2Cl. It avoids the hazards associated with the formation of chlorine azide as a potential by-product in the chlorofluorination of NaN_3 [8].

Vibrational Spectra. The infrared spectra of gaseous and Ar matrix isolated $NFCl_2$ and NF_2Cl and Raman spectra of liquid NF_2Cl and solid $NFCl_2$ were recorded. The infrared spectra of the gases were in excellent agreement with previous reports [14, 15]. Matrix infrared data had previously been reported only for NF_2Cl [16], and no Raman data had been available for either molecule. Our IR spectrum of matrix isolated NF_2Cl was in good agreement with the previous report [16], except for the antisymmetric NF_2 stretching mode, $\nu_5(a'')$, consisting only of a single band at 837 cm^{-1} and not a doublet at 842 and 837 cm^{-1}.

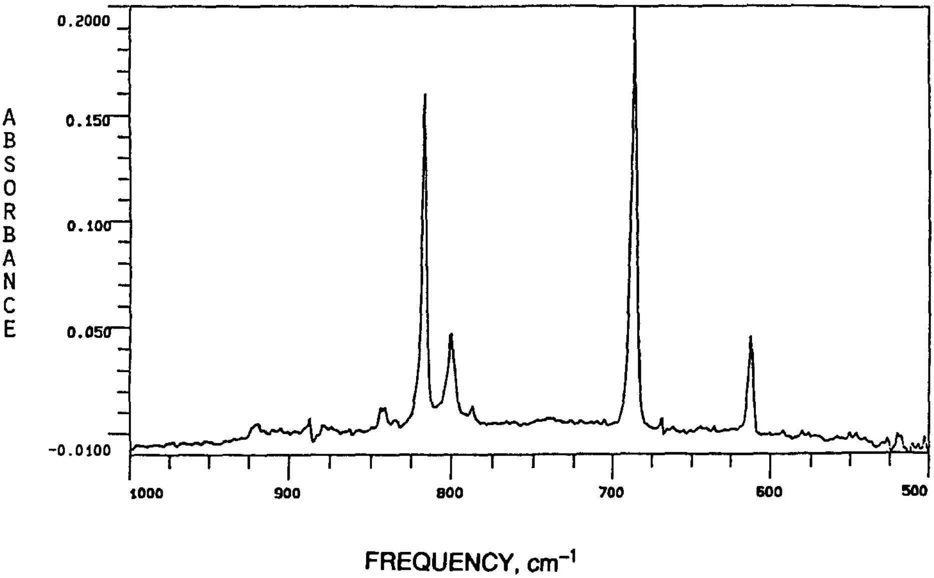

Fig 1 Infrared Spectrum of Matrix Isolated $NFCl_2$. The absorption at 800 cm^{-1} was of variable relative intensity and is due to either an impurity or a matrix effect.

In our IR spectrum of matrix isolated $NFCl_2$ (see Figure 1) the NF stretching mode, ν_1(a'), the symmetric NCl_2 stretch, ν_2(a'), and the antisymmetric NCl_2 stretch, ν_5(a"), were observed at 816, 612 and 686 cm^{-1}, respectively. The slight frequency decreases relative to the corresponding gas phase values of 833, 619 and 694cm^{-1} are comparable to those found for NF_2Cl [15,16]. Our Raman spectrum of solid $NFCl_2$ at -130°C showed the following bands: 800 (5), ν_1(a'), ν_{NF}; 689 (5), ν_5(a"), $\nu_{as}NCl_2$; 617 (33), ν_2(a'), ν_sNCl_2; 430 (100), ν_3 (a'), δ_sFNCl_2; 348 (20), ν_6(a"), $\delta_{as}FNCl_2$; 281 (35), ν_4(a'), δ_{sciss} NCl_2. The observed frequencies and relative intensities are in good agreement with the infrared data and confirm the assignments previously made [14] for the infrared spectrum of the gas.

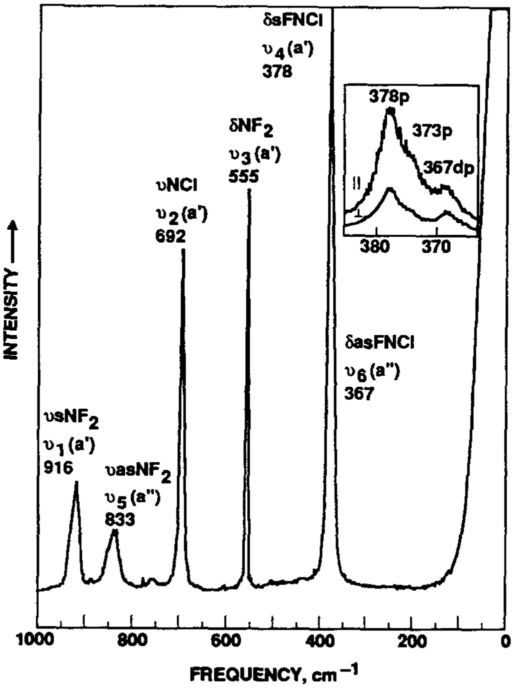

Fig 2. Raman Spectrum of liquid NF_2Cl, recorded at -150°C. The insert shows polarization data for the 378 cm^{-1} band recorded with higher resolution and scale expansion.

The Raman spectrum of liquid NF_2Cl is shown in Figure 2. For the two FNCl deformation modes, the given assignment deviates from that [16] previously proposed. As recognized correctly in the previous matrix study, the two FNCl deformation modes nearly coincide, and three bands at 382, 377 and 366 cm^{-1} had been observed. Since the antisymmetric NF_2 stretching mode, $\nu_5(a")$, had shown a 5 cm^{-1} splitting, it was assumed that the 382-377 cm^{-1} bands represent the second a" mode of NF_2Cl, with the 5cm^{-1} splittings being due to a site symmetry effect observable only for the a" modes [16]. The following observations in our study suggest that the previous assignments for the two FNCl deformations need to be reversed, i.e. that the a' FNCl deformation has a higher frequency than the a" one: (i) In our matrix IR spectrum, only a single band at 837 cm^{-1} was observed for the antisymmetric NF_2 stretching mode. (ii) The 378 cm^{-1} Raman band is clearly polarized, while the one at 367 cm^{-1} is depolarized; and (iii) the splitting of the 378 cm^{-1} band cannot be due to a matrix site symmetry effect because it was also observed for the Raman spectrum of the liquid. The splitting of the 378 cm^{-1} band might be attributed to the ^{35}Cl - ^{37}Cl isotopes, although the 5cm^{-1} separation appears rather large for a deformation mode, even if strong mixing with the N-Cl stretch is invoked.

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